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Time-resolved X-ray Absorption Spectroscopy of Copper Zinc Tin Sulfide Nanoparticles

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Introduction

Photovoltaic processes of the earth abundant and non-toxic Cu_2ZnSnS_4 (CZTS) absorber material in 3. generation solar cells can be investigated by time resolved X-ray absorption spectroscopy (TR-XAS) using a synchrotron-based X-ray source and synchronized laser excitation (pump-probe method). Such experiments require high quality CZTS [1] stabilized as a nanoparticle (NP) ink as a model system, which is also applicable for low-cost up-scalable roll-to-roll (R2R) printing.

CZTS

Kesterite structured CZTS has the best performance when the composition is Cu-poor and Zn-rich [2] within a small region on the phase diagram (figure 1), which reduces the probability for detrimental secondary phases [3]. Theoretical work has also shown that absorber materials with this composition will contain Cu-vacancies responsible for a p-doping of the semiconducting CZTS [2].

Upscaling solar cell fabrication using CZTS requires the material to be synthesized as inks for R2R printing. Oleylamine (OLA) is commonly used as ligands during hot inject synthesis to stabilize CZTS NPs (figure 2-4) [4].

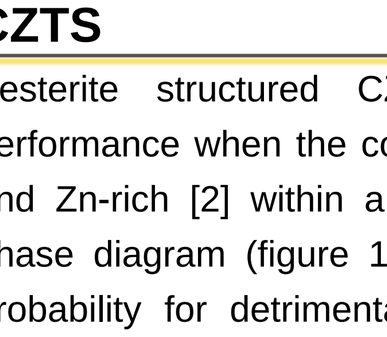

Figure 5: Band diagram of CZTS (kesterite) [9].

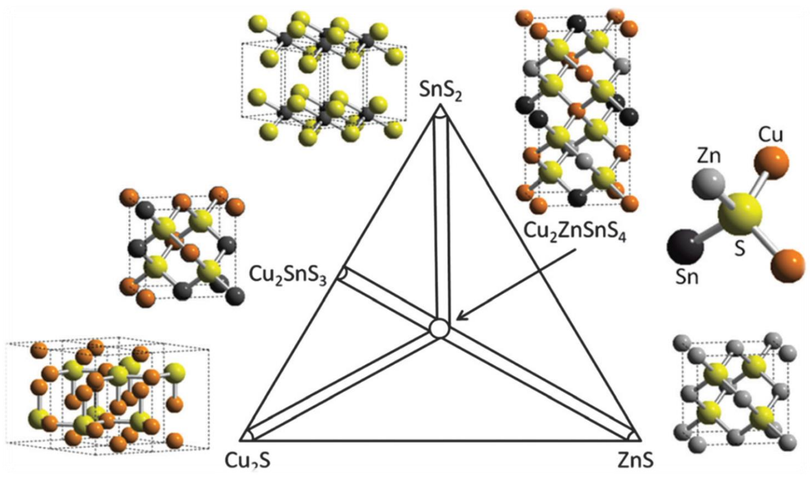

Figure 1: The pseudoternary phase diagram with the kesterite phase and other secondary phases along with their crystal structures [8].

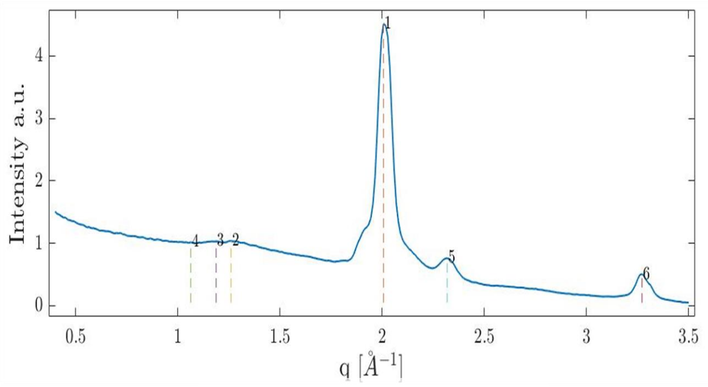

Figure 3: X-ray diffraction data showing the 112-peak for OLA-coated CZTS NPs. Using the Scherrer equation on the FWHM of the 112-peak we estimate the size of the CZTS crystals to be 13-17 nm.

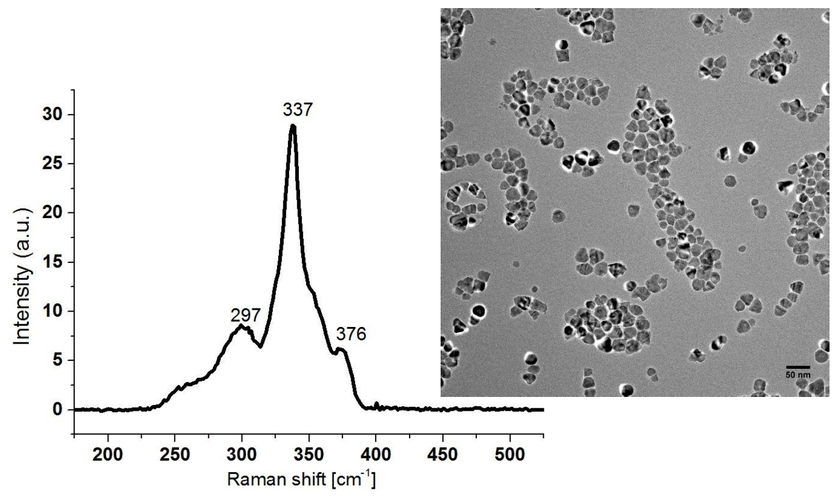

Figure 2: left – Raman spectroscopy data for OLA-coated CZTS NPs. Peaks indicate kesterite structure with no detectable signs of secondary phases. Right – TEM image.

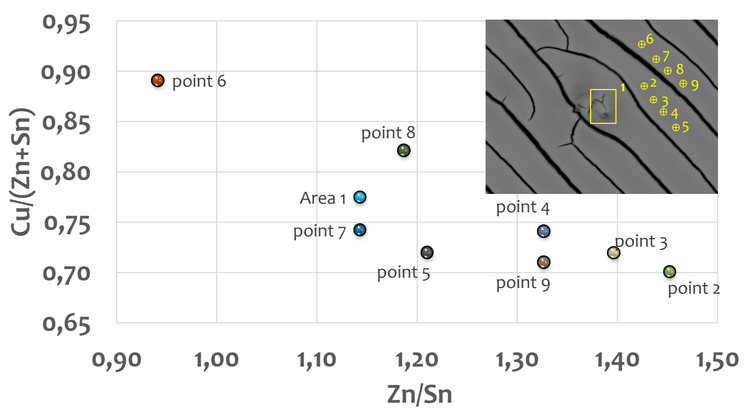

Figure 4: EDX data for OLA-coated CZTS NPs. Insert – SEM image of the samples areas on a dropcasted sample.

Probing photoexcited CZTS with TR-XAS

Upon absorbing a photon (E_{photon} > 1,5 eV) an electron is excited from the Cu-3d/S-3p* state (valence band) to the Sn-5s/S-3p* state (conduction band, Fig. 5), and photocarrier generation, localization and recombination occurs on the fs-, ps- and ns-scale, respectively [5-7]. Localization reduces mobility of charges and it is therefore important to know on what atoms these localizations occur in order to improve the efficiency of the CZTS absorber. By using TR-XAS (Fig. 6) the fate of the charge carriers in the photoexcited CZTS is interrogated at both the Cu and Zn K-edges. We have modelled the expected change in XAS near the Cu-edge for both hole and electron trapping, and is currently comparing it to experimental data (Fig 7).

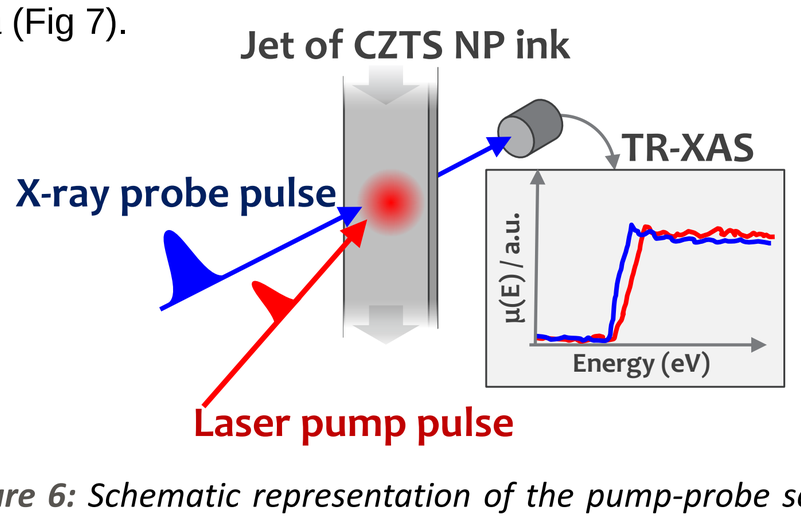

Figure 6: Schematic representation of the pump-probe scenario for the time-resolved x-ray absorption spectroscopy (TR-XAS).

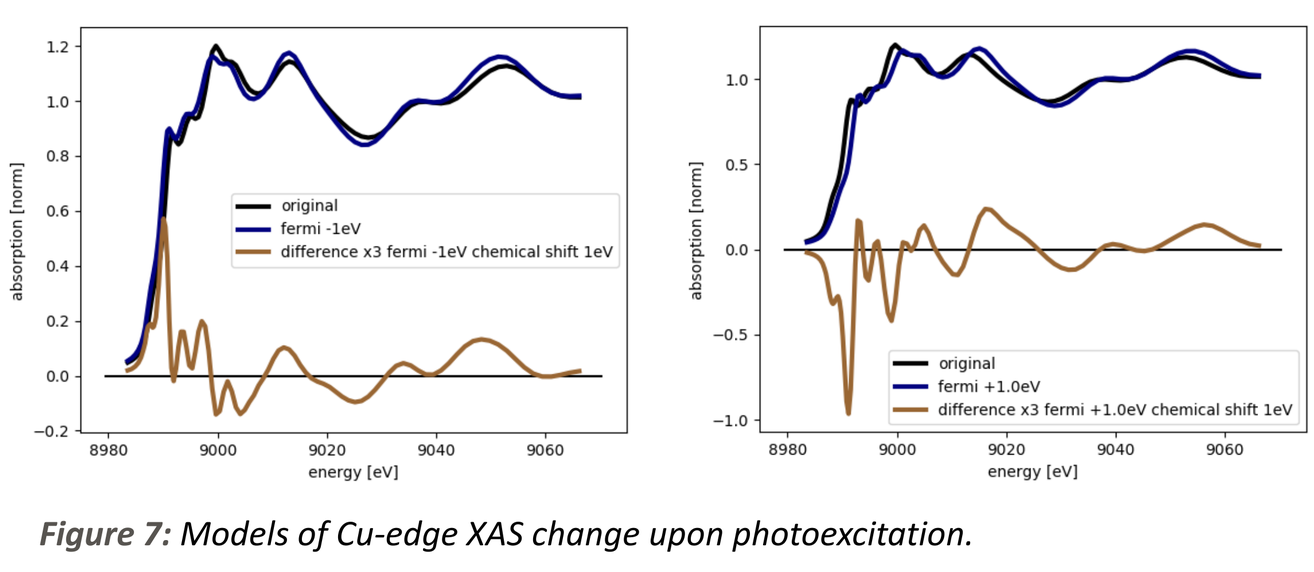

Figure 7: Models of Cu-edge XAS change upon photoexcitation.

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